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LETTERS TO THE EDITOR

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NOTES

A Fourier transform infrared study of collision induced desorption of N_2 on Ni(100) surface

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By using molecular beam technique, the translational and vibrational energy of atoms or molecules can be controlled. By collision of particles with hyperthermal kinetic energy, processes of adsorbates such as desorption, dissociation, and reaction can be induced. This phenomenon is named collision induced chemistry (CIC). Since collision induced desorption (CID) has been theoretically suggested by Zeiri *et al.*[1] and investigated experimentally by Ceyer *et al.*,[2] CIC has been examined by some groups.[3–10] In some processes of CIC, it is important to investigate the atomic collision effects on chemical states of adsorbates. In our apparatus, Fourier transform infrared (FTIR) spectra can be observed during the impingement of molecular beam. In this work, CID of N_2 from Ni(100) surface was studied with FTIR.

The experiment was carried out in a homemade molecular beam apparatus,[11] which is equipped with a FTIR spectrometer, a quadrupole mass spectrometer (QMS) for thermal desorption spectroscopy (TDS). The base pressure is 2.0×10^{-10} Torr. A supersonic molecular beam technique can be used in this apparatus. In this work, Xe atoms were seeded in He to obtain high kinetic energies for CID. The maximum kinetic energy of Xe atoms in the experiments was 1.23 eV. The incident angle of the beam was 45°. For FTIR measurements, the incident angle of infrared light to the sample was around 85°. A clean Ni(100) surface was prepared by Ne^+ ion bombardment, a 1 min annealing at 923 K.

FTIR spectra were measured after the Ni(100) surface was exposed to N_2 by backfilling the chamber with N_2 gas. At low exposures, a peak was observed at 2205 cm^{-1}. With increasing exposure, the second peak appeared at 2195 cm^{-1} and the intensity of the first peak decreased. The intensity of the second peak increased at larger exposures. These peaks are assigned to N_2 stretching modes of N_2 adsorbed molecularly at on-top sites on the surface.[12] The first peak is attributed to singleton N_2, and the second is assigned to N_2 molecules in N_2 island.[13] The interaction of N_2 molecules in the island is considered mainly both chemical interaction and dipole–dipole interaction.[14]

To estimate the coverage of N_2 remaining on the surface during CID from FTIR spectra, the relation between N_2 coverage estimated from TDS area and integrated absorbance of N_2 mode was obtained. We found that the relation was almost linear for the N_2 coverage less than 0.5. Using the relation, we estimated the N_2 coverage from the integrated absorbance.

Figure 1 shows FTIR spectra recorded continuously every 1 min after the Ni(100) $c(2\times2)$-N_2 surface (N_2 coverage is 0.5) began to be irradiated with Xe beam.[15] Xe atoms were diluted 2% in He. In this condition, the translational energy of the Xe beam was about 1.07 eV. In the figure, N_2 coverage clearly decreases with increasing Xe irradiation. After the Xe irradiation was finished, N signal in Auger electron spectra could not be detected. From these results, it was concluded that the desorption of N_2 molecules was induced by collision with the Xe beam (CID). Further, the peak po-

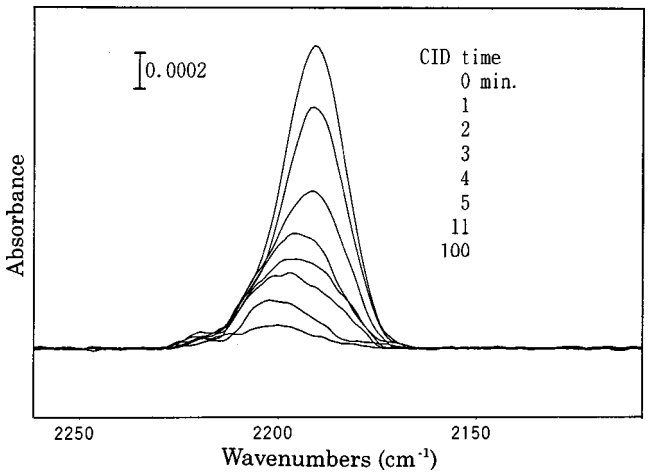

FIG. 1. FTIR spectra measured continuously every 1 min during CID of N_2 on Ni(100) by Xe atoms. The energy of Xe atoms was 1.07 eV. The Xe flux was 7.7×10^{13} atoms/cm^2·s.

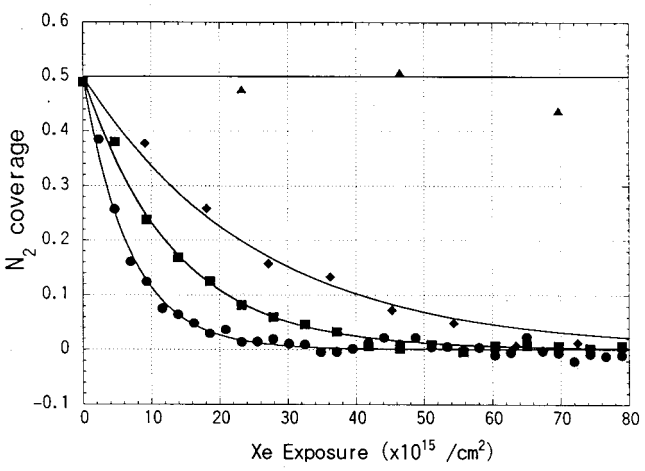

FIG. 2. Coverage of N_2 adsorbed on Ni(100) surface as a function of the exposure of Xe atoms which has a kinetic energy of 1.23 (solid circle), 1.07 (solid square), 0.93 (solid rhombus), and 0.59 (solid triangle) eV. Solid lines are fitting results in accordance with the first order rate equation.

sition shifts toward higher frequency side during CID, as shown in the figure. This tendency can be explained as follows. Before the CID experiment starts, the surface is covered with N_2 molecules. After the sample begins to be exposed to the Xe beam, Xe atoms remove N_2 molecules randomly from the surface. Then, as the Xe exposure increases, a coordination number of each N_2 molecule decreases, the interaction between them becomes weaker, and the peak position approaches that of singleton N_2. This mechanism could be observed by using FTIR with high energy resolution.

Figure 2 shows N_2 coverage estimated from FTIR spectra as a function of the amount of Xe irradiation. CID kinetics can be described as,

$$-\frac{d\theta(t)}{dt}=\sigma(E)\cdot F\cdot\theta(t), \tag{1}$$

where σ(E) is a cross section for CID, F is a flux of colliders (Xe atoms in this experiment), and $\theta(t)$ is a coverage of adsorbates (N_2 molecules in this experiment). The solid lines in the figure are the fitting results with the least square method in accordance with Eq. (1). From the results, $\sigma(E)$ can be estimated to 1.2, 0.633, 0.32, and <0.01 Å^2, for Xe energy of 1.23, 1.07, 0.93, and 0.59 eV, respectively. These results indicate that the cross section increases with increasing kinetic energy at least up to 1.23 eV. The CID mechanism, the comparison with thermal desorption, and the threshold energy analysis will be presented elsewhere.[11]

In conclusion, we studied a CID process of N_2 adsorbed on Ni(100) surface by using molecular beam technique and FTIR. The mechanism of CID was discussed from the FTIR spectra. In addition, CID cross sections were estimated from the decay of the integrated absorbance of N_2 mode in FTIR spectra. The CID cross section for Xe of 1.23 eV was 1.2 Å^2.

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[1] Y. Zeiri, J. J. Low, and W. A. Goddard III, J. Chem. Phys. **84**, 2408 (1986).
[2] J. D. Beckerle, A. D. Johnson, and S. T. Ceyer, Phys. Rev. Lett. **62**, 685 (1989).
[3] Y. Zeiri, Surf. Sci. **231**, 404 (1990).
[4] L. Romm, Y. Zeiri, and M. Asscher, J. Chem. Phys. **108**, 8605 (1998).
[5] G. Szulczewski and R. J. Levis, J. Chem. Phys. **103**, 10238 (1995).
[6] D. Velic and R. J. Levis, J. Chem. Phys. **104**, 9629 (1996).
[7] D. Velic and R. J. Levis, Surf. Sci. **396**, 327 (1998).
[8] C. Åkerlund, I. Zoric, and B. Kasemo, J. Chem. Phys. **104**, 7359 (1996).
[9] L. Vattuone, P. Gambardella, F. Cemic, U. Valbusa, and M. Rocca, Chem. Phys. Lett. **278**, 245 (1997).
[10] D. Kulginov, M. Persson, and C. T. Rettner, J. Chem. Phys. **106**, 3370 (1997).
[11] T. Takaoka, M. Terahara, M. Inamura, and I. Kusunoki (unpublished).
[12] P. A. Dowben, Y. Sakisaka, and T. N. Rhodin, Surf. Sci. **147**, 89 (1984).
[13] J. Yoshinobu, R. Zenobi, J. Xu, Z. Xu, and J. T. Yates, Jr., J. Chem. Phys. **95**, 9393 (1991).
[14] M. E. Brubaker and M. Trenary, J. Chem. Phys. **90**, 4651 (1989).
[15] S. Varma and P. A. Dowben, J. Vac. Sci. Technol. A **8**, 2605 (1990).